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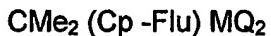
(54) Title: GROUP III BRIDGED METALLOCENE BASED ON CYCLOPENTADIENYL-FLUORENYL LIGANDS

(57) Abstract: The present invention discloses a metallocene catalyst component of formula $(Flu-R''-Cp)M(\eta^3-C_3R')_n(ether)_n$ (I) wherein Cp is a cyclopentadienyl, substituted or unsubstituted, Flu is a fluorenyl, substituted or unsubstituted, R'' is a structural bridge between Cp and Flu imparting stereorrigidity to the component, M is a metal Group III of the Periodic Table, each R' is the same or different and is hydrogen or a hydrocarbyl having from 1 to 20 carbon atoms and n is 0, 1 or 2. It further discloses a process for preparing said catalyst component and its use in the controlled polymerisation of polar or non polar monomers.

F-865 PCT**GROUP III BRIDGED METALLOCENE BASED ON CYCLOPENTADIENYL-FLUORENYL LIGANDS.**

This invention relates to the field of metallocene catalyst systems based on a cyclopentadienyl-fluorenyl component containing a metal Group III of the Periodic Table. It also relates to controlled polymerisation based on such catalyst system.

In Razavi and Ferrara (A. Razavi, J. Ferrara, J. Organomet. Chem. 435, 299, 1992), it is shown that Group IV metallocenes of the formula



wherein M is a metal Group IVB of the Periodic Table, Cp-Flu is a cyclopentadienyl-fluorenyl ligand substituted or unsubstituted, CMe₂ is a bridge between the cyclopentadienyl and the fluorenyl and wherein Q is hydrocarbon having from 1 to 20 atoms or a halogen, are effective precursors for stereospecific and stereoselective polymerization of propylene. Upon activation with an alumoxane these compounds produce high molecular weight syndiotactic polypropylene with very high activities.

On the other hand, some lanthanide alkyl and hydride complexes stabilised by cyclopentadienyl moieties have been known for about two decades to act as single component catalysts able to polymerise α -olefins (ethylene) and to initiate stereospecific polymerisation of polar monomers such as (meth)acrylates, but there is no systematic behaviour as some lanthanide complexes are active whereas others are completely unreactive. They are described for example in Ballard et al. (in D. G. H. Ballard, A. Courtis, J. Holton, J. McMeeking, R. Pearce, Chem. Commun. 1978, 994.), in Watson and Parshall (in P. L. Watson, G. W. Parshall, Acc. Chem. Res. 1985, 18, 51.), in Jeske et al. (in G. Jeske, H. Lauke, H. Mauermann, P. N. Swepston, H. Schumann, T. J. Marks, J. Am. Chem. Soc. 1985, 107, 809.), in Burger et al. (in B. J. Burger, M. E. Thompson, D. W. Cotter, J. E.

Bercaw, J. Am. Chem. Soc. 1990, 112, 1566.) or in Yasuda (in H. Yasuda, Prog. Polym. Sci. 2000, 25, 573.).

Dash et al. (in A. K. Dash, A. Razavi, A. Mortreux, C. W. Lehmann, J.-F. Carpentier, Organometallics, 2002, 21, 3238.) have worked on the amine elimination reactions of homoleptic amides $\text{Ln}[\text{N}(\text{SiMe}_3)_2]_3$ wherein Ln is yttrium, lanthanum or neodymium with the isopropylidene-bridged $\text{CpH-CMe}_2\text{-FluH}$ ligand. The resulting complex have been shown to be inactive in ethylene polymerization even upon activation with magnesium or aluminium alkyls.

Qian et al. (in C. Qian, W. Nie, J. Sun, J. Chem. Soc., Dalton Trans., 1999, 3283; and in C. Qian, W. Nie, J. Sun J. Organomet. Chem., 2001, 626, 171.) have shown that the salt metathesis reaction of $\text{LnCl}_3(\text{THF})_n$ wherein Ln is Y or Lu, with the dilithiated species of the diphenyl-carbon-bridged $\text{Cp-CPh}_2\text{-Flu}$ ligand gives the structurally characterized ionic complexes $[(\eta^5,\eta^5\text{-Cp-CPh}_2\text{-Flu})\text{LnCl}_2]^-$ $[\text{Li}(\text{THF})_4]^+$ in good yields.

Another publication by the same group (C. Qian, W. Nie, Y. Chen and J. Sun, in J. Organomet. Chem. 645, 82, 2002.) discloses that the treatment of $[(\eta^5,\eta^5\text{-Cp-CPh}_2\text{-Flu})\text{LuCl}_2]^-$ $[\text{Li}(\text{THF})_4]^+$ with $\text{LiN}(\text{SiMe}_3)_2$ afforded, in a low yield of about 13%, the neutral complex $(\eta^5,\eta^5\text{-Cp-CPh}_2\text{-Flu})\text{LuN}(\text{SiMe}_3)_2$, which was found to initiate polymerisation of caprolactone and methyl methacrylate (MMA); polymethyl methacrylate (PMMA) was produced in low activity at room temperature and contained about 60% rr dyads.

Other attempts by the same group (in C. Qian, W. Nie, Y. Chen, S. Jie, J. Organomet. Chem., 2002, 645, 82; and in W. Nie, C. Qian, Y. Chen, S. Jie, J. Organomet. Chem., 2002, 647, 114.) to extend this chemistry to "light" lanthanide metals such as for example La or Nd have failed; the successful syntheses of some

derivatives $[(\text{Cp-CPh}_2\text{-Flu})\text{Ln}((\mu\text{-H})_3\text{BH})_2]^+[\text{Li}(\text{THF})_4]^-$ wherein Ln is La or Nd, also structurally characterised, stem from steric stabilisation of the system by versatile bridging bonding of tridentate BH_4^- anions with lanthanide atom.

JP-A-07258319 discloses the preparation of the neutral carbyl complex $\{\eta^5,\eta^5\text{-Cp-CMe}_2\text{-}(2,7\text{-tBu}_2\text{-Flu})\}\text{LnCH}(\text{SiMe}_3)_2$ via a two-step, one-pot procedure involving salt metathesis between $\text{YCl}_3(\text{THF})_n$ and $\text{Li}_2[\text{Cp-CMe}_2\text{-}(2,7\text{-tBu}_2\text{-Flu})]$, followed by subsequent transmetallation with $\text{LiCH}(\text{SiMe}_3)_2$. The title complex was characterised only by ^1H NMR and claimed to initiate living polymerization of MMA at 0 °C to give a polymer with weight average molecular weight distribution M_w of 512,000, a polydispersity index D of 1.66 and 78% rr dyads. The polydispersity index D is defined by the ratio M_w/M_n of the weight average molecular weight to the number average molecular weight.

There is therefore no unified method to prepare in good yield bridged metallocene components based on cyclopentadienyl-fluorenyl ligands and on Group III metals and to prepare therefrom catalyst systems having good polymerisation capability.

In addition all known metallocene catalyst systems based on metals Group IV of the Periodic Table require costly and dangerous activating agents and are not suitable to polymerise polar monomers.

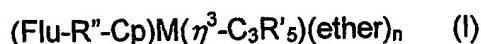
It is an aim of the present invention to prepare in good yield bridged metallocene components based on cyclopentadienyl-fluorenyl ligands and based on Group III metals.

It is another aim of the present invention to prepare catalyst components efficient in the controlled polymerisation of styrene.

It is a further aim of the present invention to prepare catalyst components capable of preparing syndiotactic polymethylmethacrylate.

More generally, the present invention aims at preparing catalyst systems efficient in the controlled polymerisation of polar or non polar monomers.

Accordingly, the present invention discloses a metallocene catalyst component of the general formula



wherein Cp is a cyclopentadienyl, substituted or unsubstituted, Flu is a fluorenyl, substituted or unsubstituted, M is a metal Group III of the Periodic Table, R'' is a structural bridge between Cp and Flu (9-position) imparting stereorrigidity to the component, each R' is the same or different and is hydrogen or an hydrocarbyl having from 1 to 20 carbon atoms and n is 0, 1 or 2.

The substituents on the cyclopentadienyl are not particularly limited, they can be the same or different and they include hydrocarbyls having from 1 to 20 carbon atoms.

The substituents on the fluorenyl are not particularly limited, they can be the same or different and they include hydrocarbyls having from 1 to 20 carbon atoms.

In the allyl group $\text{C}_3\text{R}'_5$, R' includes hydrogen or an hydrocarbyl having from 1 to 20 carbon atoms. It may also include a silyl group or a polybutadienyl chain.

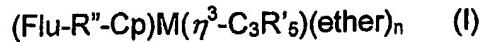
The type of bridge present between the cyclopentadienyl and the fluorenyl in the above-described catalysts is not itself particularly limited. Typically R'' comprises an alkylidene group having 1 to 20 carbon atoms, a germanium group (e.g. a dialkyl

germanium group), a silicon group (e.g. a dialkyl silicon group), a siloxane group (e.g. a dialkyl siloxane group), an alkyl phosphine group or an amine group. Preferably, the substituent comprises a silyl radical or a hydrocarbyl radical having at least one carbon atom, to form the bridge, or a substituted or unsubstituted ethylenyl radical (e.g. -CH₂CH₂-). More preferably R" is isopropylidene (Me₂C), Ph₂C, ethylenyl, or Me₂Si, and most preferably R" is (Me₂C).

M is preferably yttrium, lanthanum or a member of the lanthanide series. Throughout this description, the term "lanthanide series" means the rare earth series of elements having atomic numbers of from 58 to 71. In the lanthanide series M is preferably neodymium, samarium. More preferably, M is yttrium.

The present invention also discloses a method for preparing the catalyst component (I) that comprises the steps of:

- a) suspending MCl₃(THF)_n in ether;
- b) suspending a dilithium salt of (Cp-R"-Flu) in ether;
- c) carrying out the salt metathesis reaction of suspensions a) and b) at a temperature of from -80 °C to 60 °C, and wherein the molar ratio of suspensions b) to a) is less than 2;
- d) crystallising the product obtained in c) from the ether;
- e) retrieving a crystalline powder;
- f) allylating the crystalline powder from step e) with ClMg(C₃R'₅) or Li C₃R'₅ or any equivalent allylating reagent in a solvent at a temperature of from -80 °C to 60 °C, wherein R' is hydrogen or a hydrocarbyl having from 1 to 20 carbon atoms;
- g) retrieving a neutral complex of formula



The relative molar amounts of $MCl_3(THF)_n$ ligand and dilithium salt are preferably one to one.

The ether can be selected for example from tetrahydrofuran (THF), dioxane, diethyl oxide or diisopropyl oxide. Preferably, it is THF or diethyl oxide (Et_2O).

The solvent can be selected from an aliphatic or aromatic hydrocarbyl such as for example toluene, xylene, pentane, cyclohexane, heptane.

The crystalline powder obtained in step e) is extremely sensitive to air: it is not soluble in pentane, sparingly soluble in toluene and readily soluble in tetrahydrofuran (THF) or diethyl oxide.

X-ray diffraction studies of several suitable crystals isolated from the products of step e) and NMR studies suggested that two compounds are in equilibrium:

- a compound of formula



and

- a compound of formula



That equilibrium is schematically represented in Figure 1 that further discloses how the equilibrium is altered during allylation, and the 1H NMR spectra of the mixture of compounds (II) and (III) is represented in Figure 2 as a function of temperature.

The anion of ionic formula (III) is represented in Figure 3.

In another aspect, the present invention covers the use of metallocene component (I), with or without activating agent or transfer agent for the controlled polymerisation of polar or non polar monomers.

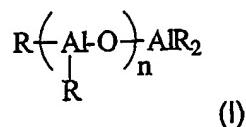
The present invention further discloses a process for homopolymerising polar or non polar monomers or for copolymerising polar or non polar monomers with a comonomer, said process comprising the steps of:

- providing the metallocene component of formula (I);
- optionally providing an activating agent or a transfer agent;
- providing a monomer and an optional comonomer;
- maintaining the system under polymerising conditions;
- retrieving the desired polymer.

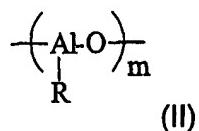
The optional activating agent includes Lewis acids having an ionising action and having a low or no co-ordinating capability. Typically, all the activators used with the metals Group IV of the Periodic Table can be used in the present invention.

Suitable aluminium-containing activating agents comprise an alumoxane or an aluminium alkyl.

The alumoxanes that can be used in the present invention are well known and preferably comprise oligomeric linear and/or cyclic alkyl alumoxanes represented by the formula (I):



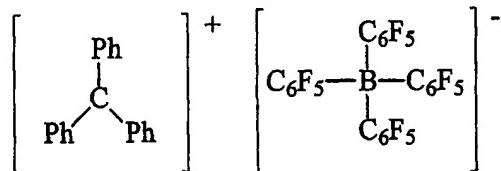
for oligomeric linear alumoxanes; and formula (II)



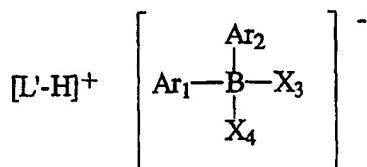
for oligomeric cyclic alumoxanes,

wherein n is 1-40, preferably 10-20; m is 3-40, preferably 3-20; and R is a C₁-C₈ alkyl group, preferably methyl. Generally, in the preparation of alumoxanes from, for example, aluminium trimethyl and water, a mixture of linear and cyclic compounds is obtained.

Suitable boron-containing activating agents may comprise a triphenylcarbenium boronate, such as tetrakis-pentafluorophenyl-borato-triphenylcarbenium as described in EP-A-0427696:



or those of the general formula below, as described in EP-A-0277004 (page 6, line 30 to page 7, line 7):



Other preferred activating agents include hydroxy isobutylaluminium and a metal aluminoxinate. These are particularly preferred when at least one Q in the general formula for metallocenes comprises an alkyl group.

Alkylating agents of the type MgR'₂ can also be used, wherein each R' is the same or different and is a hydrocarbyl having from 1 to 20 carbon atoms.

The transfer agents comprise for example H₂ and hydrosilanes of the formula HsiRⁿ₃ wherein each Rⁿ is the same or different and is either hydrogen or an hydrocarbyl having from 1 to 20 carbon atoms. It will be selected in accordance with the monomer to be polymerised.

The monomers that can be used in the present invention include non polar monomers such as for example ethylene, alpha-olefins, styrene and polar monomers such as for example acrylates or dienes. Preferably, styrene and methyl methacrylate have been used.

The catalyst system of the present invention may be employed in any type of homo- or co-polymerisation method, provided that the required catalytic activity is not impaired. In a preferred embodiment of the present invention, the catalyst system is employed in a bulk polymerisation process or in a solution polymerisation process, which is homogeneous, or in a slurry process, which is heterogeneous. In a solution process, typical solvents include THF or hydrocarbons having from 4 to 7 carbon atoms such as heptane, toluene or cyclohexane. In a slurry process, it is necessary to immobilise the catalyst system on an inert support, particularly a porous solid support such as talc, inorganic oxides and resinous support materials such as polyolefin. Preferably, the support material is an inorganic oxide in its finely divided form.

Suitable inorganic oxide materials that are desirably employed in accordance with this invention include group IIA, IIIA, IVA, or IVB metal oxides such as silica, alumina and mixtures thereof. Other inorganic oxides that may be employed, either alone or in combination with the silica or alumina, are magnesia, titania, zirconia, and the like. Other suitable support materials, however, can be employed, for example, finely divided functionalised polyolefins such as finely divided polyethylene.

Preferably, the support is a silica support having a surface area of from 200-700 m²/g and a pore volume of from 0.5-3 ml/g.

The polymerisation temperatures range from 20 °C up to 100 °C.

The present invention also covers the polymers obtainable by polymerisation in the presence of the catalysts components described hereabove.

List of Figures.

Figure 1 represents the mechanism for the formation of compounds (I), (II) and (III). In this Figure ,R represents C₃R"₅ as defined in the description.

Figure 2 represents a drawing of the crystal structure of the anion of [(η³,η⁵-Flu-CR₂-Cp)(η¹,η⁵-Flu-CR-Cp)Y]⁻[Li(ether)₄]⁺. Ellipsoids correspond to 50% probability.

Figure 3 represents the temperature dependence of the ¹H NMR spectra of the mixture obtained in step e) in THF-d₈ solution.

Examples.

Synthesis of (η⁵,η⁵-Cp-CMe₂-Flu)Y(C₃H₅)(THF).

A “one-pot” synthesis of (η⁵,η⁵-Cp-CMe₂-Flu)Y(C₃H₅)(THF) was prepared from YCl₃.

To a solution of $C_{13}H_8H-CMe_2-C_5H_4H$ (1.0 g, 3.67 mmol) in diethyl ether (50 mL) at -10°C was added under vigorous stirring 2 equiv. of *n*-BuLi (4.6 mL of a 1.6 M solution in hexane, 7.34 mmol). The reaction mixture was allowed to warm to room temperature. The solution turned dark-yellow and after 3 hours a yellow crystalline powder precipitated. To this suspension of the dilithium salt in ether cooled to -20°C was added a suspension of $\text{YCl}_3(\text{THF})_n$ (prepared from 0.72 g, 3.68 mmol of anhydrous YCl_3) in Et_2O (50 mL). Upon vigorous stirring and warming to room temperature the reaction mixture turned deep-red. The red solution was decanted from precipitate and evaporated in vacuo to give 0.8 g of deep-red powder. To a suspension of 0.390 g of the red powder of $[(\text{Cp}-CMe_2-\text{Flu})\text{YCl}_2]^-[\text{Li}(\text{Et}_2\text{O})(\text{THF})_3]^+$ in 20 mL of toluene, a solution of allylmagnesiumchloride (0.27 mL of 2M solution in THF, 0.54 mmol) was added. The reaction mixture was stirred for 8 h at room temperature. The resulting yellowish-brown solution was filtered and volatiles were removed in vacuo. The residue was washed with pentane (2×15 mL) and dried in vacuo to give a yellow powder of $(\text{Cp}-CMe_2-\text{Flu})\text{Y}(\text{C}_3\text{H}_5)(\text{THF})$ (0.16 g, 65 %). The results of the ^1H NMR (toluene- d_6 , 200 MHz, 50 $^{\circ}\text{C}$) were as follows: $\delta = 7.90$ (d, 4H, $J_{HH} = 7.0$ Hz, Flu), 7.0-6.8 (m, 4H, Flu), 5.82 (t, 1H, $J_{HH} = 2.6$ Hz, Cp), 5.59 (t, 1H, $J_{HH} = 2.6$ Hz, Cp), 3.13 (br m, 4H, α -CH₂, THF), 2.45 (br m, 2H, α -CH₂, THF), 2.24 (s, 6H, CH₃), 1.93 (br m, 4H, CH₂CHCH₂), 1.21 (br m, 4H, β -CH₂, THF). ^1H NMR (THF- d_6 , 300 MHz, -70 $^{\circ}\text{C}$): $\delta = 7.93$ (d, 2H, $J_{HH} = 7.7$ Hz, Flu), 7.63 (d, 2H, $J_{HH} = 7.7$ Hz, Flu), 7.05 (t, 2H, Flu), 6.49 (t, 2H, Flu), 6.23 (s, 2H, Cp), 5.57 (s, 2H, Cp), 4.66 (m, 1H, $J_{HH} = 13.0$ Hz, CH₂CHCH₂), 1.86 (s, 6H, CH₃), 1.52 (d, 4H, $J_{HH} = 13.0$ Hz, CH₂CHCH₂). The results of the ^{13}C NMR (THF- d_6 , 75 MHz, -70 $^{\circ}\text{C}$) were as follows: $\delta = 143.2$ (CH₂CHCH₂), 132.8, 130.8, 125.6, 120.8, 120.3, 110.3, 110.1, 107.1, 106.8, 103.7, 103.5, 98.6 (Flu and Cp), 57.7 (CH₂CHCH₂), 38.5 (CCH₃).

Polymerization of methyl methacrylate (MMA).

To a preweighted amount of about 10 mg of (*Cp-CMe₂-Flu*)Y(C₃H₅)(THF) in toluene, methyl methacrylate (3.0 mL, 27.7 mmol) was added by syringe and vigorous stirring at a temperature of -15 °C was immediately started. After a time period of one hour, the Schlenk tube was opened to air and acetone (30 mL) was added to quench the reaction and dissolve the polymer formed. The polymer was precipitated by adding methanol (ca. 200 mL), filtered, washed twice with methanol (30 mL) and dried in vacuo. The ratio [MMA]/[Y] was of about 300. The number average molecular weight Mn and the weight average molecular weight Mw were determined by GPC in THF using universal calibration relative to polystyrene standards. The molecular weight distribution is described by the polydispersity index D defined as the ratio Mn/Mw of the weight average molecular weight to the number average molecular weight. The polymer microstructure was determined by ¹H NMR in CDCl₃. The resulting polymer had a number average molecular weight Mn of 424,000, an polydispersity index D of 1.41 and the following tacticity: rr = 67 %, mr = 27 % and mm = 6 %. The yield was of 29 %.

Polymerisation of styrene.

Bulk polymerisation and solution polymerisation of styrene were carried out both with a crude sample and a recrystallised sample of (*Cp-CMe₂-Flu*)Y(C₃H₅)(THF). The conditions and results are displayed in Table I.

Table I.

complex	Condit	T (°C)	time (h)	Yield (%)	M _n (10 ³)	M _w /M _n	T _m (°C)
crude	bulk	20	1	47	nd	nd	269
crude	toluene	20	2	28	nd	nd	268
recrys	bulk	20	2	26	nd	nd	268

recrys	toluene	60	0.3	8	nd	nd
recrys	toluene	60	0.66	20	nd	nd

[Styrene]/[Y] ~ 2000.

CLAIMS.

1. A metallocene catalyst component of formula



wherein Cp is a cyclopentadienyl, substituted or unsubstituted, Flu is a fluorenyl, substituted or unsubstituted, R'' is a structural bridge between Cp and Flu imparting stereorrigidity to the component, M is a metal Group III of the Periodic Table, each R' is the same or different and is hydrogen or a hydrocarbyl having from 1 to 20 carbon atoms and n is 0, 1 or 2.

2. The metallocene catalyst component of claim 1 wherein M is yttrium, lanthanum, neodymium or samarium.

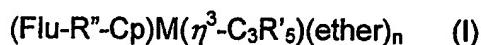
3. The metallocene catalyst component of claim 1 or claim 2 wherein R'' is CMe₂.

4. The metallocene catalyst component of any one of the preceding claims wherein C₃R'₅ is CH₂-CH=CH₂.

5. A method for preparing the catalyst component of any one of claims 1 to 4 based that comprises the steps of:

- a) suspending MCl₃(THF)_n in ether;
- b) suspending a dilithium salt of (Cp-R''-Flu) in ether;

- c) carrying out the salt metathesis reaction of suspensions a) and b) at a temperature of from -80 °C to 60 °C and wherein the molar ratio of suspension b) to suspension a) is less than 2;
- d) crystallising the product obtained in c) from the ether;
- e) retrieving a crystalline powder;
- f) allylating the crystalline powder from step e) with ClMg(C₃R'₅) or any equivalent allylating agent in a solvent at a temperature of from -80 °C to 60 °C, wherein R' is hydrogen or a hydrocarbyl having from 1 to 20 carbon atoms;
- g) retrieving a neutral complex of formula



6. The method of claim 5 wherein the molar ratio of suspension b) to suspension a) is about 1.
7. The method of claim 5 or claim 6 wherein the salt metathesis reaction is carried out at a temperature of about 20 °C.
8. The method of any one of claims 5 to 7 wherein the ether is THF or diethyl oxide.
9. The method of any one of claims 5 to 8 wherein the solvent is toluene.
10. Use of the catalyst component of any one of claims 1 to 4 with or without activating agent or transfer agent to polymerise polar or non polar monomers.
11. A process for preparing polymers comprising the steps of:
 - providing the metallocene component of any one of claims 1 to 4;

- optionally providing an activating agent and/or a transfer agent;
 - providing a polar or non-polar monomer and an optional comonomer;
 - maintaining the system under polymerising conditions;
 - retrieving the desired polymer.
12. The process according to claim 11 wherein the non polar monomer is alpha-olefin, ethylene or styrene.
13. The process according to claim 11 wherein the polar monomer is methacrylate or diene.
14. Polymers obtainable by the process according to any one of claims 11 to 13.

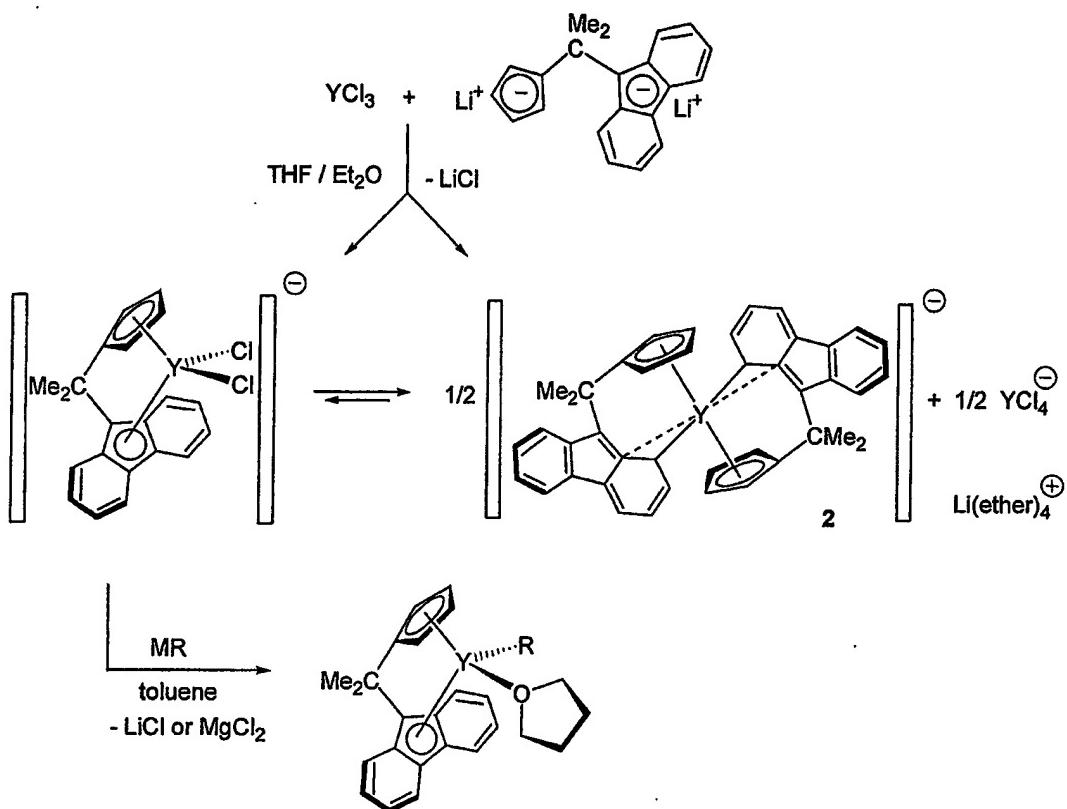


FIGURE 1

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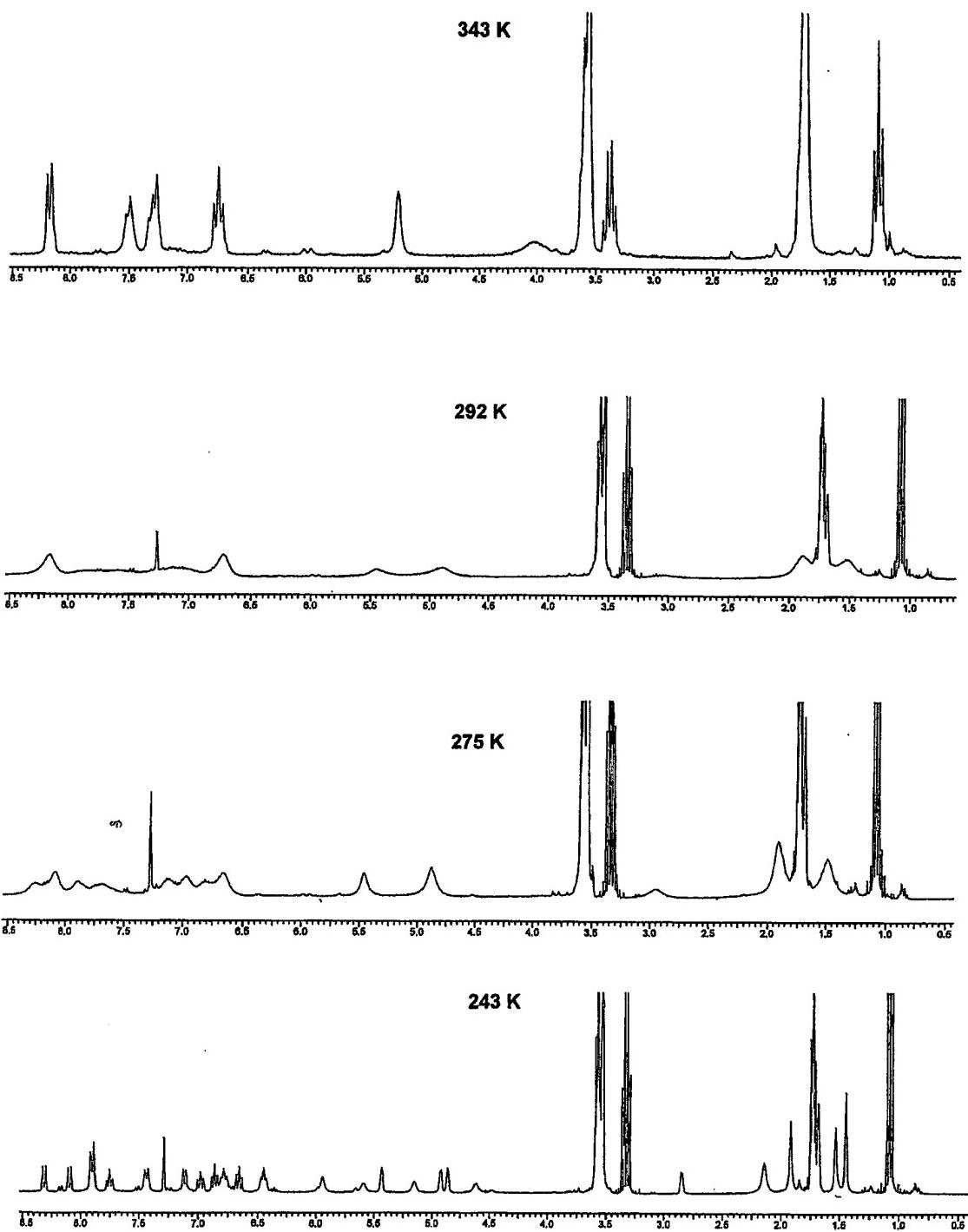


FIGURE 2

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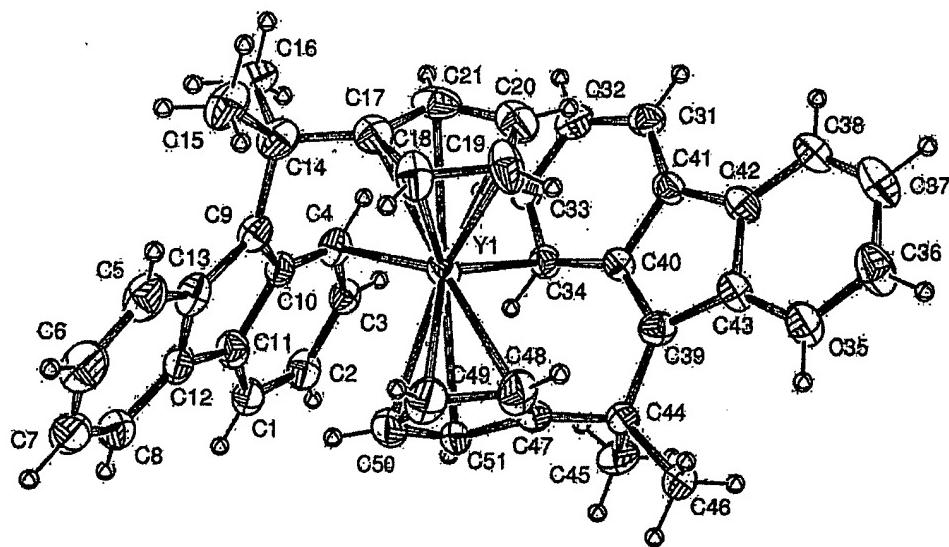


FIGURE 3

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP2004/000142

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C08F112/08 C08F4/52 C07F17/00 C08F120/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C08F C07F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, CHEM ABS Data, PAJ, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DATABASE CA [Online] CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; YASUDA, HAJIME ET AL: "Organometallic catalysts containing cyclopentadienyl group-containing fluorene derivatives and their use for polymerization of vinyl monomers" XP002257535 retrieved from STN Database accession no. 124:88161 abstract & JP 07 258319 A (MITSUBISHI RAYON CO, JAPAN) 9 October 1995 (1995-10-09) cited in the application paragraph [0029] - paragraph [0040]; claim 1 -----	1-14
X	-----	1-14

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the International filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the International filing date but later than the priority date claimed

"T" later document published after the International filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the International search

Date of mailing of the International search report

27 May 2004

24.08.2004

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Authorized officer

Parry, J

INTERNATIONAL SEARCH REPORTInternational application No.
PCT/EP2004/000142**Box II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)**

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. Claims Nos.: because they relate to subject matter not required to be searched by this Authority, namely:

2. Claims Nos.: because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:

3. Claims Nos.: because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

As a result of the prior review under R. 40.2(e), PCT,
no additional fees are to be refunded.

1. As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.

2. As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:

4. No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

1 - 4

Remark on Protest

- The additional search fees were accompanied by the applicant's protest.
 No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1-4

The subject matter of claims 1-4.

2. claims: 5-9

The subject matter of claims 5-9.

3. claims: 10-13

The subject matter of claims 10, et 11-13.

4. claim: 14

The subject matter of claims 14.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP2004/000142

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
JP 7258319	A 09-10-1995	NONE	